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March 13, 2002

## BOX PCT

Commissioner for Patents  
Washington, D.C. 20231

PCT/JP00/06047  
-filed September 6, 2000

Re: Application of Fumihiko YAMAGUCHI, Makoto HANAZAWA, and Kazunori HAYASHI  
GRAFT POLYMER, PROCESS FOR PREPARING THE SAME, AND SOLVENT-BASED WATER-AND OIL-REPELLENT COMPOSITION  
Assignee: DAIKIN INDUSTRIES, LTD.  
Our Ref: Q68929

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

- an executed Declaration and Power of Attorney.
- an English translation of the International Application.
- an English translation of Article 34 Amendment
- Notification Concerning Submission or Transmittal or Priority Document.
- an executed Assignment and PTO 1595 form.
- an Information Disclosure Statement and PTO 1449 form with references.
- International Search Report and references cited in the ISR.

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee, after entry of the Article 34 Amendment is calculated as follows:

Total claims	4	-	20	=	x \$18.00	=	\$0.00
Independent claims	1	-	3	=	x \$84.00	=	\$0.00
Base Fee							\$890.00
<b>TOTAL FILING FEE</b>							<b>\$890.00</b>
<b>Recordation of Assignment</b>							<b>\$ 40.00</b>
<b>TOTAL FEE</b>							<b>\$930.00</b>

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National Stage Entry of PCT/JP00/06047  
Q68929

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Checks for the statutory filing fee of \$890.00 and Assignment recordation fee of \$40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

Country

Japan

Application No

260186/1999

Filing Date

September 14, 1999

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Abraham J. Rosner'.

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## DESCRIPTION

GRAFT POLYMER, PROCESS FOR PREPARING THE SAME, AND  
SOLVENT-BASED WATER- AND OIL-REPELLENT COMPOSITION

## 5 FIELD OF THE INVENTION

The present invention relates to a graft polymer, a process for preparing the same, and a solvent-based water- and oil-repellent composition comprising the same.

## 10 RELATED ART

In view of regulation of fluorocarbons and environmental problems, solvents for water- and oil-repellent products, for example, halogen solvents such as R113 are being replaced by petroleum solvents. However, 15 problems such as solidification or deposition of products at low temperature arise even if the solvent is merely replaced. When the water- and oil-repellent product is diluted with the petroleum solvent having low solubility such as solvent having a small content of an aromatic 20 compound, problems such as deposition or concentration distribution arise.

When the fluorine concentration in an active component of the water- and oil-repellent agent is reduced to impart high product stability and high 25 dilution stability to the water- and oil-repellent

composition, the water- and oil-repellency is lowered.

Japanese Patent Kokoku Publication No. 50082/1986 discloses a water- and oil-repellent comprising a graft copolymer obtained by the graft copolymerization which 5 utilizes the reactivity of an OH group. However, the graft copolymer is insufficient in water repellency because a hydroxyl group is remained in the polymer.

Japanese Patent Kokai Publication No. 228534/1994 discloses a water- and oil-repellent comprising a 10 fluorine-containing graft copolymer. However, the fluorine-containing graft copolymer is insufficient in solubility in the petroleum solvent because its trunk polymer is a fluorine-containing polymer.

15 SUMMARY OF THE INVENTION

An object of the present invention is to give a graft copolymer which has high water- and oil-repellency regardless of a small fluorine content, and also has both a solubility in a petroleum solvent and a repellency 20 effect.

The present inventors have discovered that a graft polymer, wherein a branch polymer is a fluorine-containing polymer and a trunk polymer contains a fluorine-free (hydrocarbon) polymer as a main component, 25 has high water-repellency and good solubility in a

petroleum solvent.

The present invention provides a graft copolymer wherein a branch polymer having a fluoroalkyl group is bonded to a trunk polymer through a linkage having a  $-\text{C}(=\text{O})\text{NH}-$  group.

The present invention also provides a solvent-based water- and oil-repellent composition comprising the graft copolymer.

The graft polymer of the present invention is a graft polymer wherein a branch polymer is grafted at an isocyanate group moiety of a trunk polymer.

The trunk polymer has a repeating unit derived from an isocyanate group-containing vinyl monomer and a repeating unit derived from the other copolymerizable monomer.

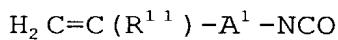
The isocyanate group, which exists in the repeating unit derived from the isocyanate group-containing vinyl monomer, reacts with an active hydrogen group of the branch polymer, thereby to bond to the branch polymer.

The term "isocyanate group-containing vinyl monomer" means a compound having a carbon-carbon double bond and an isocyanate group. The numbers of the carbon-carbon double bond and of the isocyanate group in the isocyanate group-containing vinyl monomer are generally 1. A molecule of the isocyanate group-containing vinyl monomer

usually has a carbon-carbon double bond at one terminal of the molecule and an isocyanate group at the other terminal of the molecule.

The isocyanate group-containing vinyl monomer

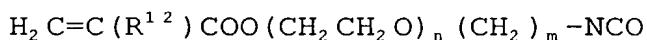
- (i) an isocyanate group-containing (meth)acrylate ester,
- (ii) a vinyl isocyanate represented by the formula:



wherein  $R^1$  is H or a linear, branched or cyclic hydrocarbon group (for example, an alkyl group) having 1 to 20 (for example, 1 to 10) carbon atoms and  $A^1$  is a direct bond or a hydrocarbon group having 1 to 20 carbon atoms, and

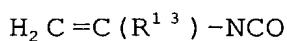
(iii) a reaction product of (iii-1) a compound having two isocyanate groups and (iii-2) a compound having a carbon-carbon double bond and an active hydrogen.

Examples of the isocyanate group-containing (meth)acrylate ester (i) include:



20 wherein R<sup>1,2</sup> is H or CH<sub>3</sub>, n is from 0 to 20, and m is from 1 to 20 (for example, 2-isocyanatoethyl (meth)acrylate).

Examples of the vinyl isocyanate (ii) include:



wherein  $R^1$  is a linear, branched or cyclic hydrocarbon  
25 group (for example, an alkyl group or a cycloalkyl group)

having 1 to 20 (for example, 1 to 10) carbon atoms,

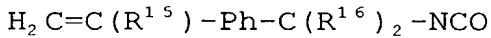


wherein  $R^{14}$  is H or a linear, branched or cyclic

hydrocarbon group (for example, an alkyl group or a

5 cycloalkyl group) having 1 to 20 (for example, 1 to 10)

carbon atoms, and n is from 2 to 20, and



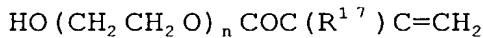
wherein  $R^{15}$  is H or  $CH_3$ ,  $R^{16}$  is H or  $CH_3$ , and Ph is a

phenylene group.

10 Examples of the compound having two isocyanate groups (iii-1) include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, diphenylmethane diisocyanate, naphthalene diisocyanate, hexamethylene diisocyanate, xylene diisocyanate, and isophorone diisocyanate.

15 Examples of the compound having a carbon-carbon double bond and an active hydrogen (iii-2) (hereinafter referred to as a "monomer having an active hydrogen") include:

hydroxyethyl (meth)acrylate,



wherein  $R^{17}$  is H or  $CH_3$  and n is from 2 to 20, and

aminoethyl (meth)acrylate.

20 The reactin between the compound having two isocyanate groups (iii-1) and the monomer having active hydrogen (iii-2) may be conducted in a solvent

(especially, an aprotic solvent, for example, an ester solvent) optionally using a catalyst such as dibutyltin dilaurate. The amount of the monomer having active hydrogen (iii-2) in the reaction may be from 1.0 to 2.0 equivalents, and preferably from 1.0 to 1.7 equivalents, based on the compound having two isocyanate groups (iii-1).

The amount of the isocyanate group-containing vinyl monomer is from 1 to 30% by weight, and preferably from 2 to 10% by weight, based on the trunk polymer.

The other copolymerizable monomer constituting the trunk polymer may be any one as far as it is an addition-polymerizable monomer (namely, a compound having a carbon-carbon double bond), and may be either of a fluorine-free monomer and a fluorine-containing monomer. The amount of the fluorine-containing monomer is at most 50% by weight, and preferably at most 10% by weight, based on the trunk polymer. The fluorine-containing monomer may not exist in the trunk polymer.

The fluorine-free monomer includes, for example, a (meth)acrylate ester. The (meth)acrylate ester may be an ester of (meth)acrylic acid and an aliphatic alcohol, for example, a monohydric alcohol or a polyhydric alcohol (for example, a dihydric alcohol).

Examples of the fluorine-free monomer include:

(meth)acrylates such as 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, hydroxyalkyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, polyoxyalkylene (meth)acrylate, 5 3-chloro-2-hydroxypropyl (meth)acrylate, glycidyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, benzyl (meth)acrylate glycidyl methacrylate, hydroxypropyl monomethacrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-10 hydroxyethyl acrylate, glycerol monomethacrylate,  $\beta$ -acryloyloxyethyl hydrogensuccinate,  $\beta$ -methacryloyloxyethyl hydrogenphthalate, 2-acryloyloxyethylhexahydrophthalic acid, 2-acryloyloxyethylphthalic acid, 2-acryloyloxyethyl-2-hydroxyethyl-15 phthalic acid, methacrylic acid hydroxypropyltrimethylammonium chloride, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, 2-acryloyloxyethyl acid phosphate, glycosyl ethyl methacrylate, methacrylamide, 2-hydroxy-3-acryloyloxypropyl methacrylate, 2-methacryloyloxyethyl acid phosphate, and hydroxypivalic acid 20 neopentyl glycol diacrylate; styrenes such as styrene and p-isopropylstyrene; (meth)acrylamides such as (meth)acrylamide, diacetone (meth)acrylamide, N-methylol (meth)acrylamide, N-butoxymethylacrylamide, and 25 2-acrylamide-2-methylpropanesulfonic acid; and vinyl

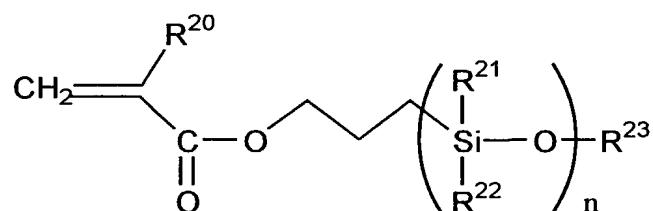
ethers such as vinyl alkyl ether.

Examples thereof further include ethylene, butadiene, vinyl acetate, chloroprene, vinyl halide such as vinyl chloride, vinylidene halide, acrylonitrile, 5 vinyl alkyl ketone, maleic anhydride, N-vinylcarbazole, vinyl pyrrolidone, and (meth)acrylic acid.

The fluorine-free monomer may be a silicon-containing monomer (for example, (meth)acryloyl group-containing alkylsilane, (meth)acryloyl group-containing 10 alkoxy silane, and (meth)acryloyl group-containing polysiloxane).

Examples of the silicon-containing monomer include: (meth)acryloxytrialkylsilane, (meth)acryloxytrialkoxy silane, (meth)acryloxypropyltrialkylsilane, (meth)acryloxypropyltrialkoxy silane, (meth)acryloxypropylpolysiloxane, 15 allyltrialkylsilane, allyltrialkoxy silane, allylpoly siloxane, vinyltrialkylsilane, vinyltrialkoxy silane, and vinylpolysiloxane.

20 The (meth)acryloxypropylpolysiloxane may be



wherein  $R^{20}$  is H or  $CH_3$ ,  $R^{21}$  is H or  $CH_3$ ,  $R^{22}$  is H or  $CH_3$ ,  $R^{23}$  is H or  $CH_3$ , and n is from 1 to 100  
(for example, (meth)acryloxypropylpolydimethylsiloxane).

5 At least two types of the fluorine-free monomers can also be used in combination.

Examples of the fluorine-containing monomer constituting the trunk polymer may be the same as those (for example, fluoroalkyl group-containing (meth)acrylate, 10 fluorinated olefin) of the fluorine-containing monomer constituting the following branch polymer. The fluorine-containing monomer may be, for example, a fluorine-containing methacrylate or acrylate.

The trunk polymer may be a block polymer or a random 15 polymer.

The branch polymer is formed by using a chain transfer agent, a fluoroalkyl group-containing vinyl monomer and, if necessary, the other fluorine-containing monomer and fluorine-free monomer.

20 The chain transfer agent may be a chain transfer agent having an active hydrogen group at both terminals, for example, an alkylenethiol chain transfer agent having an active hydrogen group or an aryl chain transfer agent having an active hydrogen group. Examples of the active 25 hydrogen group include OH,  $NH_2$ ,  $SO_3H$ ,  $NHOH$ , COOH, and SH.

The number of carbon atoms of the alkylene group of the alkylthiethiol may be from 1 to 20.

Examples of the alkylthiethiol chain transfer agent include the followings.

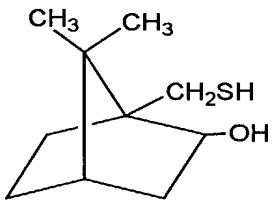
5  $\text{HS}(\text{CH}_2)_n\text{OH}$  [n is 2, 4, 6 or 11],

$\text{HSCH}_2\text{COOH}$ ,

$\text{HSCH}_2\text{CH}(\text{CH}_3)\text{COOH}$ ,

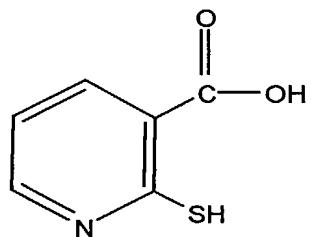
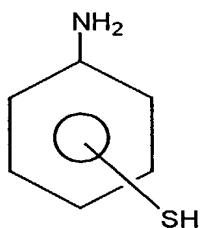
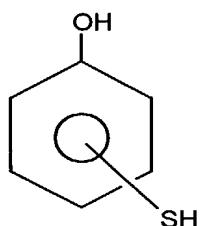
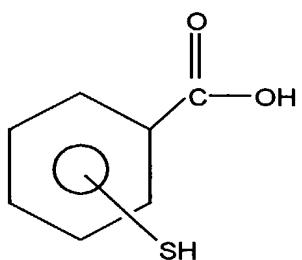
$\text{HSCH}_2\text{CH}_2\text{SO}_3\text{Na}$ ,

$\text{HSCH}_2\text{CH}_2\text{SO}_3\text{H}$ , and



10

Examples of the allyl chain transfer agent include the followings.



agent reacts with an isocyanate group of the trunk polymer to form a  $-\text{NH}-\text{C}(=\text{O})-$  linkage (an amide linkage). When the active hydrogen group is a OH group, it forms an urethane linkage  $(-\text{NH}-\text{C}(=\text{O})-\text{O}-)$ . When the active hydrogen group is an  $\text{NH}_2$  group, it forms an urea linkage  $(-\text{NH}-\text{C}(=\text{O})-\text{NH}-)$ . The amount of the isocyanate group of the trunk polymer is preferably from 1.0 to 2.0 equivalents, for example, from 1.0 to 1.7 equivalents, based on 1.0 equivalents of the chain transfer agent.

10 The amount of the chain transfer agent may be from 0.05 to 0.7 mol, preferably from 0.1 to 0.6 mol, based on 1 mol of the branch monomer. The chain transfer agent is bonded at one terminal of the branch polymer obtained by polymerizing the branch monomer. The chain transfer agent can control the length of a chain of the branch polymer.

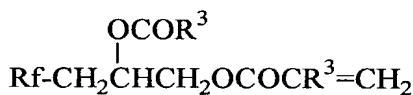
15 The fluoroalkyl group-containing vinyl monomer, which constitutes the branch polymer, may be (meth)acrylate having a fluoroalkyl group.

20 The fluoroalkyl group-containing (meth)acrylate may be represented by the following general formula:



25 wherein Rf is a fluoroalkyl group having 3 to 21 carbon atoms,  $\text{R}^{1\ 8}$  is hydrogen or a methyl group, and  $\text{A}^2$  is a divalent organic group.

Examples of the fluoroalkyl group-containing (meth)acrylate include:



5

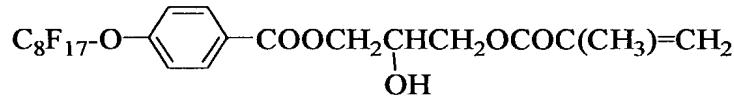
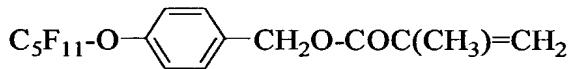
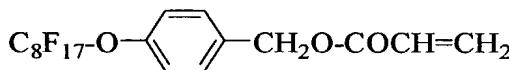


wherein Rf is a fluoroalkyl group having 3 to 21 carbon atoms, R<sup>1</sup> is hydrogen or an alkyl group having 1 to 10 carbon atoms, R<sup>2</sup> is an alkylene group having 1 to 10 carbon atoms, R<sup>3</sup> is hydrogen or a methyl group, Ar is

arylene group which optionally has a substituent group, and n is an integer of 1 to 10.

Specific examples of the fluoroalkyl group-containing (meth)acrylate include the followings.

5       $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)\text{OCOCH}=\text{CH}_2$  ,  
 $\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)\text{OCOC(CH}_3\text{)}=\text{CH}_2$  ,  
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_6(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$  ,  
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OCOC(CH}_3\text{)}=\text{CH}_2$  ,  
 $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$  ,  
10      $\text{CF}_3(\text{CF}_2)_7\text{SO}_2\text{N(CH}_3\text{)}(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$  ,  
 $\text{CF}_3(\text{CF}_2)_7\text{SO}_2\text{N(C}_2\text{H}_5\text{)}(\text{CH}_2)_2\text{OCOC(CH}_3\text{)}=\text{CH}_2$  ,  
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CH(OCOCH}_3\text{)}\text{CH}_2\text{OCOC(CH}_3\text{)}=\text{CH}_2$  ,  
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_8\text{CH}_2\text{CH(OH)}\text{CH}_2\text{OCOCH}=\text{CH}_2$  ,  
 $\text{CF}_3\text{C}_6\text{F}_{10}(\text{CF}_2)_2\text{SO}_2\text{N(CH}_3\text{)}(\text{CH}_2)_2\text{OCOCH}=\text{CH}_2$  ,



15



As a matter of course, at least two types of the fluoroalkyl group-containing (meth)acrylates can be used

in combination.

In the branch polymer, the other fluorine-containing monomer may be used. The other fluorine-containing monomer includes a fluorinated olefin (having, for example, 3 to 20 carbon atoms), for example,  $\text{CF}_3(\text{CF}_2)_7\text{CH}=\text{CH}_2$ .

In the branch polymer, a fluorine-free monomer may be used. Examples of the fluorine-free monomer used in the branch polymer include the same fluorine-free monomers as those used in the trunk polymer. The fluorine-free monomer in the branch polymer may be a (meth)acrylate ester, for example, an ester of an aliphatic monohydric alcohol and (meth)acrylic acid.

The amount of the fluorine-free monomer in the branch polymer may be at most 80% by weight, e.g. at most 50% by weight, particularly at most 30% by weight, based on the branch polymer.

The branch polymer may be a block polymer or a random polymer. The polymerization degree of the branch polymer is from 3 to 25 molecules, and preferably from 4 to 20 molecules of the monomer, based on one molecule of the chain transfer agent.

The graft polymer comprises the trunk polymer and the branch polymer. A weight ratio of the trunk polymer to the branch polymer may be from 5:95 to 95:5,

preferably from 10:90 to 90:10, particularly from 30:70 to 70:30.

The number average molecular weight (by GPC, converted to polystyrene, in THF) of the graft polymer 5 may be from 5,000 to 200,000, preferably from 5,000 to 100,000.

The graft polymer of the present invention may be prepared by either of:

(A) a method of copolymerizing macromonomer, which is obtained by reacting an isocyanate group-containing vinyl monomer with a branch polymer, and a copolymerizable monomer (a trunk monomer) to form a trunk polymer (a method of polymerizing a trunk monomer in the presence of a branch polymer), and

15 (B) a method of reacting a trunk polymer, which is obtained by copolymerizing an isocyanate group-containing vinyl monomer and a copolymerizable monomer, with a branch polymer (a method of separately polymerizing a branch polymer and a trunk polymer).

20 The method (A) comprises the steps of:

(A-1) polymerizing a chain transfer agent and a fluoroalkyl group-containing vinyl monomer, which are constituent components of a branch polymer, and, if necessary, the other fluorine-containing monomer and a fluorine-free monomer to give a branch polymer; and

(A-2) reacting the resultant branch polymer with an isocyanate group-containing vinyl monomer to give a macromonomer; and

(A-3) polymerizing a macromonomer and a copolymerizable monomer constituting a trunk polymer to give a graft polymer.

The method (B) comprises the steps of:

(B-1) polymerizing an isocyanate group-containing vinyl monomer and a copolymerizable monomer, which are constituent components of a trunk polymer, to give an NCO group-containing trunk polymer; and

(B-2) grafting a separately synthesized branch polymer onto the resultant trunk polymer to give a graft polymer.

The polymerization step (A-1) of the branch polymer and the polymerization steps (A-3) and (B-1) of the trunk polymer may be conducted in a solvent at a temperature of 70 to 80°C using a polymerization initiator. The polymerization time is generally from 2 to 12 hours.

As the polymerization initiator, for example, azobisisobutyronitrile, benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene hydroperoxide, tert-butyl peroxide pivalate, and diisopropylperoxy dicarbonate are used. The amount of the polymerization initiator is preferably from 1 to 10 parts by weight based on 100 parts by weight of the monomer.

The polymerization solvent may be a polar solvent, a hydrocarbon solvent, or a mixture of these solvents. When the isocyanate group exists in the reaction system (namely, in the steps (A-2), (B-1) and (B-2)), a protic solvent having an active hydrogen group such as alcohol solvent can not be used.

The polar solvent is a solvent having a polar group in a molecule. Examples of the polar group include a hydroxyl group, a carboxyl group, an ester group, an acyl group, and an ether oxygen group. Examples of the polar solvent include an alcohol solvent, a glycol solvent, an ester solvent, and a ketone solvent.

The hydrocarbon solvent may be a solvent which is composed only of carbon and hydrogen. The hydrocarbon solvent may be an aliphatic hydrocarbon. Examples of the hydrocarbon solvent include n-heptane, n-hexane, n-octane, cyclohexane, methylcyclohexane, cyclopentane, methylcyclopentane, methylpentane, 2-ethylpentane, isoparaffin hydrocarbon, liquid paraffin, decane, undecane, dodecane, mineral spirit, and mineral terpene. In some case, an aromatic solvent may be used.

Examples of the alcohol solvent include butyl alcohol and isopropyl alcohol. Examples of the glycol solvent include propylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene

glycolmonomethyl ether, dipropylene glycol monoethyl ether, and acetate thereof. Examples of the ester solvent include a monobasic acid ester such as methyl acetate, ethyl acetate, and butyl acetate; and a dibasic acid ester such as diethyl succinate, diethyl adipate, dibutyl phthalate, and dioctyl phthalate. Examples of the ketone solvent include methyl isobutyl ketone (MIBK), methyl ethyl ketone, and acetone.

A mixture of the hydrocarbon solvent and the polar solvent may also be used. The weight ratio of the hydrocarbon solvent to the polar solvent may be from 100:0 to 0:100, for example 5:95 to 95:5.

The reaction steps (A-2) and (B-2) of reacting the active hydrogen group of the chain transfer agent constituting the branch polymer with the isocyanate group contained in the monomer constituting the trunk polymer may be conducted in a solvent at a temperature of 30°C to 65°C. The reaction time is generally from 2 hours to 24 hours.

Although the solvent may be the polymerization solvent described above, a protic solvent having an active hydrogen group such as alcohol solvent can not be used.

An organic solvent solution of the graft polymer is a solvent-based water- and oil-repellent composition.

The water- and oil-repellent composition of the present invention may contain other water- and oil-repellents and additives, for example, softening agents, antistatic agents, cross-linking agents and crease-proofing agents, if necessary.

A substrate to be treated with the water- and oil-repellent composition of the present invention includes various substances. Examples of the substrate to be treated include textiles, glass, papers, woods, hides, asbestos, bricks, cements, metals and oxides, ceramics, plastics, coated surfaces, and plasters. Examples of the textiles include animal- and vegetable-origin natural fibers such as cotton, hemp, wool, and silk; synthetic fibers such as polyamide, polyester, polyvinyl alcohol, polyacrylonitrile, polyvinyl chloride, and polypropylene; semisynthetic fibers such as rayon and acetate, etc.; and a mixture of these fibers. The water- and oil-repellent composition of the present invention is applied to the substrate by a method of applying the composition onto the surface of the substrate to be treated using a known process such as dip coating, and then drying the composition.

The water- and oil-repellent composition of the present invention can also be used as an aerosol by adding propellants. Examples of preferred propellant

include fluoroalkane or chlorofluoroalkane having 1 or 2 carbon atoms, LPG gas, dimethyl ether, nitrogen gas, and carbon dioxide gas. Typical examples of the fluoroalkane or chlorofluoroalkane having 1 or 2 carbon atoms include  
5 dichlorodifluoromethane, trichlorotrifluoroethane, chlorodifluoromethane, chlorodifluoroethane, dichloro-  
trifluoroethane, tetrafluoroethane, and a mixture of at  
least two types of them. The amount of the propellant is  
preferably 0.05 to 2 times as much as the total weight of  
10 the surface treating agent composition containing the  
solvent.

A container having a mechanism for spraying a liquid in the container, for example, an aerosol container or a spray container is filled with the aerosol.

15

#### PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be illustrated by the following Examples which do not limit the present invention.

20

Characteristics were determined as follows.

#### Water- and Oil-repellency

A polymer solution is diluted with a mineral spirit so that a solid content of the solution is 0.8% by weight, and then sprayed over a cloth using a hand spray so that  
25 the cloth is sufficiently wetted. As the cloth, a

polyester cloth, a polyester/cotton mixed spun cloth and a cotton cloth are used. After drying at room temperature for 10 hours, the water repellency and oil repellency are evaluated in the following procedures.

5 The water repellency is expressed by the water repellency No. (cf. the following Table 1) determined by the spray method according to JIS (Japanese Industrial Standard)-L-1092 (1998).

10 The oil repellency is determined by dropping several drops of a test solution shown in Table 2 on the surface of a test cloth and then observing the penetration state of the drops after 30 seconds (AATCC-TM118).

15

Table 1

Water repellency No.

State

5	No wet on the surface
4	Slight wet on the surface
3	Partial wet on the surface
2	Wet on the surface
1	Wet over the whole surface

Table 2

Oil repellency	Test solution	Surface tension (dyne/cm, 25°C)
8	n-Heptane	20.0
7	n-Octane	21.8
6	n-Decane	23.5
5	n-Dodecane	25.0
4	n-Tetradecane	26.7
3	n-Hexadecane	27.3
2	n-Hexadecane/Nujol (35/65 by weight)	29.6
1	Nujol	31.2
0	Inferior to 1	-

Product stability

After adjusting the concentration of the polymer solution to 15% by weight using a mineral spirit, the polymer solution is stored at -5°C for one month. It is evaluated whether or not solidification or deposition occurs.

○: Homogeneous liquid is maintained.

×: Solidification or deposition occurs.

Dilution stability

The polymer solution is diluted with a solvent (n-decane) so that the solid content of the solution is 0.8% by weight, and then stored at -5°C for one month. It is

evaluated whether or not solidification or deposition occurs.

O: Homogeneous and transparent liquid is maintained.

Δ: Some turbidity occurs, but homogeneous liquid is maintained for practical use.

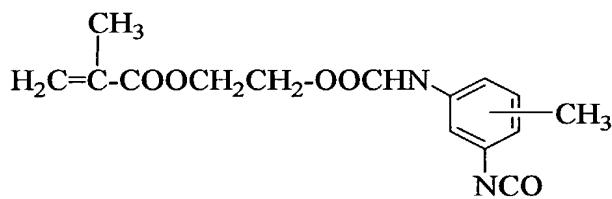
5

\*: Deposition or solidification occurs.

### Synthesis Example 1

## (Synthesis of isocyanate group-containing vinyl monomer)

10 In a 500 ml three-necked flask equipped with a  
dropping funnel, 100 g of 2,4-tolylene diisocyanate, 100  
g of ethyl acetate and 0.1 g dibutyltin dilaurate were  
charged. While shaking at 50 to 55°C, 90 g of  
hydroxyethyl methacrylate and 90 g of ethyl acetate were  
15 added dropwise through the dropping funnel over 15  
minutes and the mixture was reacted for 8 hours to give  
an isocyanate group-containing vinyl monomer (a) shown  
below:



20

Example 1

In a 1,000 ml glass polymerization sample, the following components were charged and reacted in a nitrogen atmosphere at 75°C for 8 hours while shaking to give a branch polymer.

Mercaptoethanol	3 g
CF <sub>3</sub> CF <sub>2</sub> (C <sub>2</sub> F <sub>4</sub> ) <sub>n</sub> C <sub>2</sub> H <sub>4</sub> OCOCH=CH <sub>2</sub> (FA) [n = 3.5 in average]	95 g
Stearyl methacrylate(StMA)	5 g
Azoisobutyronitrile	0.17 g
Ethyl acetate	120 g

After the completion of the reaction, a gas chromatography analysis revealed that 100% of monomers were consumed. A NMR analysis revealed that a composition ratio (molar ratio) of the respective components in the polymer, namely, a ratio of mercaptoethanol:FA:StMA was 1.0:4.8:0.8.

After reducing the temperature to 55 to 60°C, 9 g of 2-isocyanatoethyl methacrylate (2-EHMA) and 0.1 g of dibutyltin dilaurate were charged in an air atmosphere and the reaction was conducted at 55 to 60°C for 8 hours while shaking to give a macromonomer. After the completion of the reaction, an absorption peak of a NCO group of an IR spectrum nearly disappeared.

To the macromonomer, the following components were

added and the reaction was conducted in a nitrogen atmosphere at 75°C for 8 hours while shaking to give a graft polymer.

2-Ethylhexyl methacrylate (2EHMA)	100	g
Maleic anhydride (MAN)	10	g
Ethyl acetate	515	g
Tert-butyldperoxy pivalate (Perbutyl PV, manufactured by NOF Corp.)	9	g

5 After the completion of the reaction, a gas chromatography analysis revealed that 100% of monomers were consumed. A GPC analysis revealed that a number average molecular weight of the resultant polymer was 8,000.

10 The water- and oil-repellency, the product stability  
and the dilution stability of the resultant polymer  
solution were determined. The results are shown in Table  
5.

### Example 2

15 In the same manner as in Example 1, except that 38 g  
of the solution (50% by weight) of isocyanate group-  
containing vinyl monomer (a) prepared in Synthesis  
Example 1 was used in place of 2-isocyanatoethyl  
methacrylate, the synthesis was conducted.

20 In the preparation of each of the branch polymer and  
the graft polymer, 100% of monomers were consumed. After

the completion of the reaction for forming a macromonomer, an NCO absorption of an IR spectrum nearly disappeared. A GPC analysis revealed that a number average molecular weight of the resultant polymer was 8,500.

5 The water- and oil-repellency, the product stability  
and the dilution stability of the resultant polymer  
solution were determined. The results are shown in Table  
5.

### Examples 3 to 6

10 The same procedure as in Example 1 was repeated,  
except that the monomers shown in Table 3 were used.

In the preparation of each of the branch polymer and the graft polymer, 100% of monomers were consumed. After the completion of the reaction for forming a macromonomer, 15 an NCO absorption of an IR spectrum nearly disappeared. A GPC analysis revealed that a number average molecular weight of the resultant polymers was 9,300 in Example 3, 9,000 in Example 4, 8,600 in Example 5, and 8,000 in Example 6.

20 The water- and oil-repellency, the product stability  
and the dilution stability of the resultant polymer  
solutions were determined. The results are shown in  
Table 5.

### Comparative Example 1

25 1.0 equivalent of 2-isocyanatoethyl methacrylate

and 0.7 equivalents of mercaptoethanol were reacted in ethyl acetate at 50°C for 12 hours in the presence of 0.1 g of dibutyltin dilaurate.

To 5.5 g of the resultant reaction product (a reaction product of an isocyanate group-containing vinyl monomer and mercaptoethanol), the following components were added and the mixture was reacted in a nitrogen atmosphere at 75°C for 8 hours while shaking to give a polymer.

CF <sub>3</sub> CF <sub>2</sub> (C <sub>2</sub> F <sub>4</sub> ) <sub>n</sub> C <sub>2</sub> H <sub>4</sub> OCOCH=CH <sub>2</sub> (FA) [n = 3.5 in average]	42.7 g
Stearyl methacrylate (StMA)	2.3 g
2-Ethylhexyl methacrylate (2EHMA)	45.0 g
Maleic anhydride (MAN)	4.5 g
Ethyl acetate	515 g
Tert-butyperoxy pivalate (Perbutyl PV, manufactured by NOF Corp.)	9 g

The resultant polymer was not a graft polymer. A GPC analysis revealed that a number average molecular weight of the resultant polymer was 15,000.

The water- and oil-repellency, the product stability and the dilution stability of the resultant polymer solution were determined. The results are shown in Table 5.

#### Comparative Example 2

The same procedure as in Comparative Example 1 was

repeated, except for using, as a reaction product of the isocyanate group-containing vinyl monomer and mercaptoethanol, a reaction product obtained by reacting a reaction mixture of 1.0 equivalent of the isocyanate group-containing vinyl monomer (a) of Synthesis Example 1 with 0.7 equivalents of mercaptoethanol in ethyl acetate at 50°C for 12 hours and using the monomers shown in Table 4.

The resultant polymer was not a graft polymer. A GPC analysis revealed that a number average molecular weight of the resultant polymer was 14,000.

The water- and oil-repellency, the product stability and the dilution stability of the resultant polymer solutions were determined. The results are shown in Table 5.

#### Comparative Example 3 to 6

The same procedure as in Comparative Example 1 was repeated, except that the monomers shown in Table 4 were used.

The polymers obtained in Comparative Examples 3 to 6 were not a graft polymer. A GPC analysis revealed that a number average molecular weight of the resultant polymers was 18,000 in Comparative Example 3, 16,000 in Comparative Example 4, 19,500 in Comparative Example 5, and 16,000 in Comparative Example 6.

The water- and oil-repellency, the product stability and the dilution stability of the resultant polymer solutions were determined. The results are shown in Table 5.

Table 3: Amount (g) of monomer

	Branch polymer				Macromonomer			Trunk polymer	
	Mercapto-ethanol	FA	StMA	2-EHMA	THFMA	2-Isocyanato-ethyl methacrylate	Isocyanate group-containing vinyl monomer (a)	2-EHMA	MAN
Example 1	3	95	5	-	-	9	-	100	10
Example 2	3	95	5	-	-	-	38	100	10
Example 3	3	95	5	-	-	9	-	110	-
Example 4	3	90	10	-	-	9	-	100	10
Example 5	3	90	-	10	-	9	-	100	10
Example 6	3	90	-	-	10	9	-	100	10

(Note)

FA:  $\text{CF}_3\text{CF}_2(\text{C}_2\text{F}_4)_n\text{C}_2\text{H}_4\text{OCOCH}=\text{CH}_2$ ,  $n = 3.5$  in average

StMA: stearyl methacrylate

2-EHMA: 2-ethylhexyl methacrylate

THFMA: tetrahydrofurfuryl methacrylate

MAN: maleic anhydride

Isocyanate group-containing vinyl monomer (a): 50 wt% solution of isocyanate group-containing vinyl monomer (a) of Synthesis Example 1

Table 4: Amount (g) of monomer

	FA	StMA	2-EHMA	THFMA	MAN	Reaction product of isocyanate group-containing vinyl monomer and mercaptoethanol
Comp. Example 1	42.7	2.3	45.0	—	4.5	5.5
Comp. Example 2	40.9	2.2	43.2	—	4.3	9.4
Comp. Example 3	42.7	2.3	49.5	—	—	5.5
Comp. Example 4	40.5	4.5	45.0	—	4.5	5.5
Comp. Example 5	40.5	—	49.5	—	4.5	5.5
Comp. Example 6	40.5	—	45.0	4.5	4.5	5.5

(Note)

FA:  $\text{CF}_3\text{CF}_2(\text{C}_2\text{F}_4)_n\text{C}_2\text{H}_4\text{OCOCH}=\text{CH}_2$ ,  $n = 3.5$  in average

StMA: stearyl methacrylate

2-EHMA: 2-ethylhexyl methacrylate

THFMA: terahydrofuryl methacrylate

MAN: maleic anhydride

Table 5

	Water-repellency			Oil-repellency			Product stability	Dilution stability
	Polyester	Polyester/cotton	Cotton	Polyester	Polyester/cotton	Cotton		
Example 1	5	5	5	5	6	6	O	O
Example 2	5	5	4	4	6	6	O	O
Example 3	5	3	3	2	3	3	O	O
Example 4	5	5	5	5	6	6	O	O
Example 5	5	5	5	5	6	5	O	O
Example 6	5	5	5	5	5	3	O	O
Comp. Example 1	2	2	1	1	1	0	x	x
Comp. Example 2	1	1	1	0	0	0	x	x
Comp. Example 3	2	2	1	0	0	0	O	x
Comp. Example 4	2	2	1	1	1	0	x	x
Comp. Example 5	2	1	1	2	1	0	x	x
Comp. Example 6	2	1	1	2	2	2	O	x

### Effect of the Invention

The graft polymer of the present invention can exhibit both the function of the fluorine-containing component and that of the hydrocarbon component. For 5 example, it is possible to reconcile the softness of treated articles (especially, textiles) with the repellency effect of the water- and oil-repellency and to reconcile the solubility of the water- and oil-repellent with the repellency effect.

10 Furthermore, high water- and oil-repellency can be imparted even when a small amount of the water- and oil-repellent is used. Good performances can be exhibited even if the content of the fluoroalkyl group-containing vinyl monomer in the graft polymer is small.

amended on August 27, 2001

## CLAIMS

1. (amended) A graft copolymer wherein a branch polymer having a fluoroalkyl group is bonded to a trunk polymer through a linkage having a  $-C(=O)NH-$  group,  
5 wherein the linkage having a  $-C(=O)NH-$  group is formed by reacting an active hydrogen group of a chain transfer agent constituting the branch polymer with an isocyanate group contained in a monomer constituting the trunk polymer.

10

2. (deleted)

3. (amended) A solvent-based water- and oil-repellent composition comprising the graft copolymer of claim 1.

15

4. A process for preparing the graft copolymer of claim 1, which comprises copolymerizing a macromonomer, which is obtained by reacting an isocyanate group-containing vinyl monomer with a branch polymer, and a copolymerizable monomer to form a trunk polymer.  
20

25 5. A process for preparing the graft copolymer of claim 1, which comprises reacting a trunk polymer, which is obtained by copolymerizing an isocyanate group-containing vinyl monomer and a copolymerizable monomer, with a branch

polymer.

10/070978

## ABSTRACT

A graft polymer, which is obtained by grafting a branch polymer having a fluoroalkyl group onto a trunk polymer through a linkage having a  $-\text{C}(=\text{O})\text{NH}-$  group, gives a solvent-based water- and oil-repellent composition having high water- and oil-repellency, high product stability and high dilution stability.

**DECLARATION AND POWER OF ATTORNEY FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)**

As a below named inventor, I hereby declare that: My residence, mailing address, and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**GRAFT POLYMER, PROCESS FOR PREPARING THE SAME, AND SOLVENT-BASED  
WATER- AND OIL-REPELLENT COMPOSITION**

the application of which

is attached hereto

OR

was filed on September 6, 2000 as ~~NON-PCT INTERNATIONAL APPLICATION~~  
~~NUMBER~~ PCT International Application Number PCT/JP00/06047,  
(Confirmation No.       ), and was amended on  
August 27, 2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified application, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part application(s), material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application(s) which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application(s) having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date	Priority Claimed Yes	No
<u>260186/1999</u>	<u>Japan</u>	<u>September 14, 1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>

I hereby claim domestic priority benefits under 35 United States Code §120 of any United States application(s), §119(e) of any United States provisional application(s), or §365(c) of any PCT International application(s) designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in a listed prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge my duty to disclose any information material to the patentability of this application as defined in 37 C.F.R. 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Prior U.S. or International Application Number(s)	U.S. or International Filing Date	Status

I hereby appoint all attorneys of **SUGHRUE MION, PLLC** who are listed under the USPTO Customer Number shown below as my attorneys to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith, recognizing that the specific attorneys listed under that Customer Number may be changed from time to time at the sole discretion of Sughrue Mion, PLLC, and request that all correspondence about the application be addressed to the address filed under the same USPTO Customer Number.



23373

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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